ASSESSMENT OF Fe_2O_3/SiO_2 CATALYSTS FOR THE CONTINUOUS TREATMENT OF PHENOL AQUEOUS SOLUTIONS IN A FIXED BED REACTOR

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Abstract

Different iron-containing catalysts have been tested for the oxidation of phenol aqueous solutions in a catalytic fixed bed reactor in presence of hydrogen peroxide. All the catalysts consist of iron oxide, mainly crystalline hematite particles, over different silica supports (mesostructured SBA-15 silica and non-ordered mesoporous silica). The immobilization of iron species over different silica supports was addressed by direct incorporation of metal during the synthesis or post-synthesis impregnation. The synthesis conditions were tuned up to yield agglomerated catalysts with iron loadings between 10 and 15 wt. %. The influence of the preparation method and the type of silica support was evaluated in a catalytic fixed bed reactor for the continuous oxidation of phenol in terms of its activity (phenol and total organic carbon degradation) as well as its stability (catalyst deactivation by iron leaching). Those catalyst prepared by direct synthesis either in presence (Fe_2O_3/SBA-15(DS)) or absence (Fe_2O_3/SiO_2(DS)) of template molecules achieved high catalytic performances (TOC reduction of 65 and 52 %, respectively) with remarkable low iron leaching in comparison with the impregnated iron catalysts. Catalytic results demonstrated that the synthesis method plays a crucial role in the dispersion and stability of active species and hence resulting in superior catalytic performances.

1. Introduction

The degradation of aromatic pollutants in wastewater streams generated by industrial processes has emerged as an important concern due to the restrictive environmental laws and regulations. Phenol and phenol-like compounds show high toxicity for microorganisms, high chemical oxygen demand and poor biodegradability. Advanced Oxidation Processes (AOPs) are postulated as interesting alternatives for the destruction of organic pollutants in industrial wastewaters. These processes involve the generation of non-selective and highly reactive hydroxyl radical ($^{\bullet}OH$), which is one of the most powerful oxidation agents [1], higher than others chemical oxidants commonly used in wastewater treatments.

The use of hydrogen peroxide as oxidant is an option commercially available for the treatment of industrial wastewaters [2,3]. Nevertheless, the hydrogen peroxide by itself is not effective at high concentrations of refractory compounds due to the reaction rate is very low, even for high oxidant concentrations [4]. In order to promote the generation of hydroxyl radicals and reduce secondary reactions, the use of catalytic processes, such as Fenton systems, could be interesting alternatives. The reaction of hydrogen peroxide with ferrous salts (Fenton's reagent) or other low-valence transition metals (Fenton-like reactions) at room temperature are well known sources of hydroxyl radicals [5]. In some cases, temperature has been increased up to 80-120 ºC leading to the so-called Catalytic Wet Hydrogen Peroxide Oxidation (CWHPO) processes. The homogeneous oxidation of organic compounds by means of Fenton-like reactions has been studied in numerous works during last years and it is commercially used to treat industrial wastewaters [6]. However, these homogeneous systems present two main drawbacks. Firstly, the hydroxyl radical production by Fenton-like reactions is strongly dependent on limited pH range (2.5-3.5) and secondly, a final separation of soluble iron species from the treated wastewater is needed.

These drawbacks have promoted the development of Fenton and CWHPO processes based on heterogeneous catalytic systems. The catalyst design is usually a key factor in order to increase its surface area, minimize the metal sintering, improve its chemical stability and govern the useful lifetime of the catalyst. Therefore, several studies have been addressed to the

incorporation of active iron species over different supports, such as silica, zeolites [7-8], hexagonal mesostructured materials (MCM-41, HMS 9 and SBA-15) [9-13], as well as pillared clays [14] for its application in CWHPO. An interesting overview of solid catalysts is reported by Perathoner and Centi [15], in which Al-Fe-clays are shown as one group of the most promising catalysts. More recently, the same authors have stated that copper pillared clays are highly effective for WHPO of wastewater streams from olive oil milling production with low loss of copper by leaching [16]. Melero et al. [11] have also reported a remarkable catalytic performance of a novel Fe_2O_3/SBA-15 composite catalyst as compared to homogeneous systems as well as a low dependence on the pH for the treatment of phenolic aqueous solutions.

These heterogeneous processes have been carried out in batch operations and phenol is frequently used as model pollutant. The use of solid catalysts for CWHPO indicates a good perspective of this technology for its application in continuous processes, but it still requires large engineering efforts in modelling and optimal designing of catalyst and industrial reactors. Moreover, their application in continuous systems is normally questioned by the catalyst fouling, in particular for the treatment of wastewater with a complex composition. On the other hand, for its application in fixed bed reactors, catalysts must be shaped into bodies such as granules, spheres and extrudates, in order to decrease the pressure drop and to achieve a convenient mechanical strength. However, there is almost no information in the open literature about its agglomeration process, although this is an essential step regarding its commercial application. Therefore, few works are described in literature dealing with the treatment of organic pollutants by means of a fixed bed reactor using hydrogen peroxide as oxidant. In this sense, a major experience of continuous processes can be found in catalytic wet air oxidation. In this context, the aim of this contribution has been the study of the influence of several supports and iron incorporation methods for the degradation of phenol aqueous solutions using a continuous CWHPO process.

2. Experimental

2.1. Preparation of powder and extruded Fe/SiO_2 materials

Several powder silica-supported iron materials were prepared following two different methods: direct incorporation of the metal during the synthesis and post-synthesis incipient wetness impregnation. In the first strategy, iron was incorporated by direct co-condensation of the silica (TEOS) and iron ($FeCl_3 \cdot 6H_2O$) sources during the synthesis of: i) mesostructured SBA-15 materials with hexagonal mesoscopic order (Fe_2O_3/SBA-15(DS)) following the method described elsewhere [17] and ii) non-ordered silica support synthesized by means of the sol-gel method, based on acid-catalysed hydrolysis and basic condensation with ammonium hydroxide (Fe_2O_3/SiO_2(DS)). The second method based on the incipient wetness impregnation with $Fe(NO_3)_3 \cdot 9H_2O$ aqueous solution was carried out over: i) silica SBA-15 material (Fe_2O_3/SBA-15(I)), SiO_2 sol-gel (Fe_2O_3/SiO_2(I)) and commercial silica from PQ Corporation (Fe_I/SiO_2-PQ(I)). With the purpose of comparison, a physical mixture of hematite iron oxide (Fe_2O_3; Aldrich) with the mesostructured SBA-15 silica (Fe_2O_3+SBA-15(PM)) was also prepared. Prior to the agglomeration of the powder catalysts, all the materials were calcined at 550 ºC for 5 hours.

Fe/SiO_2 extrudates were prepared by blending of the powder catalyst with sodium bentonite (75:25 wt %) and synthetic methylcellulose polymer (10 wt. % of the previous mixture) which act as binders in the extrusion process [18]. All the components were kneaded with deionised water under high shear conditions until obtaining a homogeneous paste, which was conditioned in a damp atmosphere. Thereafter, the paste was pushed through a ram extruder of 4.8 mm circular die and the resultant rod-shaped materials were dried for 3 days in a climatic chamber under controlled temperature and relative humidity (RH) from 20 ºC and 70 % RH to 40 °C and 10 % RH. Finally, the extrudates were calcined in air until 650 °C (2 hours) using a slow ramp of temperature, in order to achieve a gradual removal of water and the organic content, strengthening the mechanical consistence of the material by sintering of the inorganic binder. The final pellets for the catalytic reactions were crushed and sieved until particle sizes with spherical-like shape and an average diameter between 1.6 and 2 mm.

2.2. Catalysts characterization

Physicochemical and textural properties as well as the presence of crystalline phases of the powder materials and extruded catalysts were analyzed by means of different conventional techniques. X-ray powder diffraction (XRD) data were acquired on a Philips X-Pert diffractometer using Cu Kα radiation. The data were collected ranging 2θ from 0.5 to 50º with a resolution of 0.02º. Nitrogen adsorption and desorption isotherms at 77 K were measured using a Micromeritics Tristar 3000 System. Transmission electron microscopy (TEM) images were taken on a Philips Tecnai-20 electron microscope operating at 200 kV. SEM images were obtained in a XL30 ESEM FEI (PHILIPS) electron microscope. The iron content of the synthesised materials was measured by means of Atomic Emission Spectroscopy with Induced Coupled Plasma (ICP-AES) analysis collected in a Varian Vista AX system.

2.3. Catalytic tests in an up-flow fixed bed reactor

Fig. 1 depicts the experimental set-up used for the degradation of phenol aqueous solutions by means of Catalytic Wet Hydrogen Peroxide Oxidation (CWHPO). The tubular reactor was made of glass with inner diameter of 1.2 cm and 15 cm of length. The catalyst particles were packed between glassy beads to enable a better distribution of the inlet solution inside the catalyst bed and achieve the desired temperature. The operation conditions for the evaluation of the activity and stability of the synthesized materials were set according to preliminary studies with this experimental set-up [19]: i) reactor temperature of 80 ºC, ii) 1 mL/min of feed flow rate, iii) 1 g/L of phenol concentration and 5.1 g/L of H_2O_2 (stoichiometric amount for the complete phenol mineralization, according to the reaction (1)) in the inlet solution, and iv) 2.9 g of catalyst with a particle size between 1.6 and 2 mm.

$$C_6H_5OH + 14H_2O_2 \rightarrow 6CO_2 + 17H_2O \qquad (1)$$

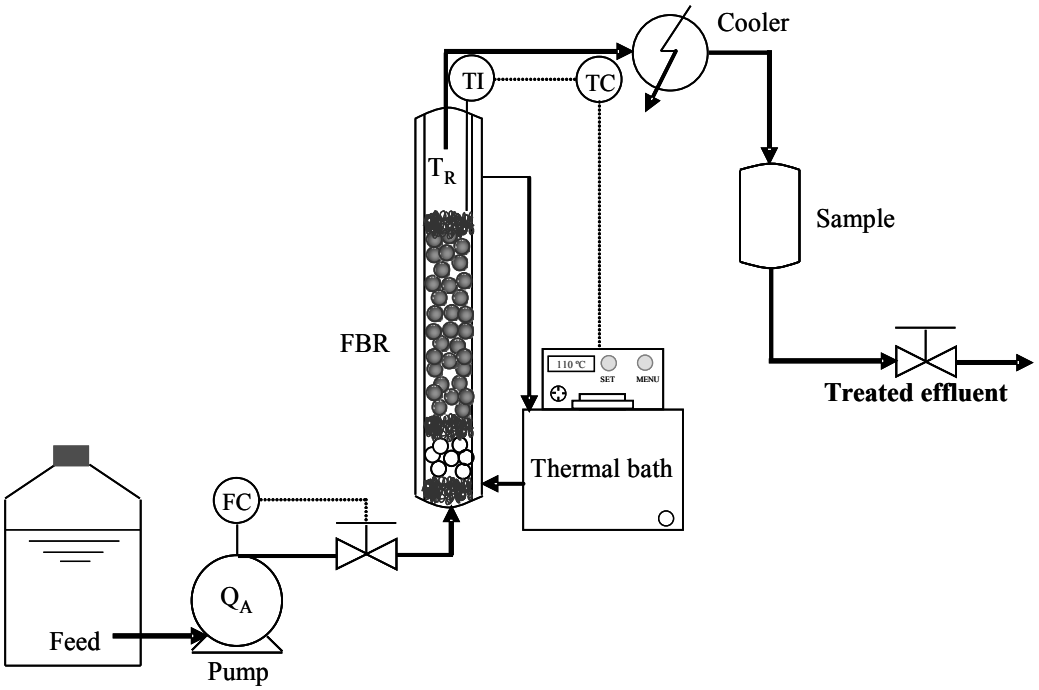

Fig. 1. Experimental set-up of the up-flow fixed bed reactor for the catalytic wet hydrogen peroxide oxidation of phenol aqueous solutions.

Samples were hourly withdrawn from the treated effluent to determine Total Organic Carbon (TOC), phenol and hydrogen peroxide concentrations, as well as iron leached out from the catalyst to the treated effluent. TOC content of the solutions was analysed using a combustion/non dispersive infrared gas analyser model TOC-V Shimadzu. Phenol conversion was determined by means of HPLC chromatograph (Varian Prostar) equipped with a Waters Spherisorb column and an UV detector adjusted at 215 nm, employing ultrapure water acidified with H_3PO_4 up to pH 2.7 as mobile phase. Hydrogen peroxide conversion was determined by iodometric titration. Iron content in the treated solution was measured by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analysis collected in a Varian VISTA AX system.

3. Results and discussion

3.1. Catalysts characterization

Table 1 shows the physicochemical properties of the synthesized powder and extruded iron catalysts, as well as the silica materials used as supports for impregnation. The materials have been classified in different groups depending on the silica support: mesostructured SBA-15, mesoporous silica obtained via sol-gel and commercial extruded mesoporous silica acquired from PQ Corporation. As can be seen, the first group corresponds to hexagonal mesostructured SBA-15 materials, where iron was incorporated by direct synthesis (Fe_2O_3/SBA-15(DS)) and incipient wetness impregnation (Fe_2O_3/SBA-15(I)). Additionally, physical mixture of hematite iron oxide and the SBA-15 silica support (Fe_2O_3+SBA-15(PM)) was also prepared. The second group includes mixed Fe_2O_3-SiO_2 materials synthesized by simultaneous condensation of iron and silica sources via the sol-gel method (Fe_2O_3/SiO_2(DS)) or impregnation of mesoporous silica sol-gel (Fe_2O_3/SiO_2(I)). Finally, the third group is constituted by impregnated commercial silica support (Fe_2O_3/SiO_2-PQ(I)).

Table 1. Characterization data of iron-containing catalysts supported over silica materials.

Material (Synthesis method)	Support	Powder			Extruded		
		S_{BET} (m^2/g)	Vp (cm^3/g)	Fe (wt. %)	S_{BET} (m^2/g)	Vp (cm^3/g)	Fe (wt. %)
SBA-15	**SBA-15**	790	1.21	-	-	-	-
Fe_2O_3/SBA-15(I)		549	0.78	15.8	333	0.53	12.4
Fe_2O_3/SBA-15(DS)		475	0.67	18.0	264	0.48	14.0
Fe_2O_3+SBA-15(PM)		-	-	-	277	0.49	13.8
SiO_2	**SiO_2 sol-gel**	296	1.79		-	-	
Fe_2O_3/SiO_2(I)		207	0.85	15.9	180	0.62	12.0
Fe_2O_3/SiO_2(DS)		270	0.69	14.8	225	0.55	11.1
SiO_2-PQ	**SiO_2 PQ**	-	-	-	346	1.16	-
Fe_2O_3/SiO_2–PQ(I)		-	-	-	252	0.87	15.4

Characterization data of powder materials evidence that catalysts based on SBA-15 silica supports have higher specific surface areas than those supported over the silica synthesized via sol-gel. This is due to the narrow pore size distribution of mesoporous SBA-15 channels (7-9

nm) with hexagonal arrangement, which provides remarkable surface areas and pore volumes (650-800 m^2/g and 1-1.2 cm^3/g, respectively). In contrast, silica sol-gel materials depict broader pore size distributions and higher average pore diameter than SBA-15 based materials, which lead to higher ratio between pore volume and specific surface area. As result of the iron incorporation process over both silica supports, a significant reduction of surface area and pore volume were evidenced for all the catalysts, although this fact was particularly more accentuated for the incorporation of iron by direct synthesis over SBA-15 materials (Fe_2O_3/SBA-15(DS)) [20]. Nevertheless, the powder catalysts synthesized over SBA-15 supports show higher specific surface areas regardless of the synthesis method (475 and 550 m^2/g, for Fe_2O_3/SBA-15(DS) and Fe_2O_3/SBA-15(I), respectively) than the counterparts supported over non-ordered mesoporous silica (270 and 207 m^2/g for Fe_2O_3/SiO_2(DS) and Fe_2O_3/SiO_2(I), respectively).

XRD patterns illustrated in Fig. 2 evidence typical diffractions of the hexagonal arrangement of mesoporous materials for powder iron containing SBA-15 catalysts in the low angle range, whereas iron catalyst prepared by sol-gel method or impregnation over silica sol-gel does not show any sign of mesoscopic order. At higher angles, clear diffraction peaks at 33, 36 and 42 º are observed, which are characteristic of crystalline hematite iron oxide particles, except for Fe_2O_3/SBA-15(I) catalyst. This fact could be related to the small size of the crystalline iron oxide particles which makes less visible to the X ray diffraction. The comparison between XRD pattern of powder and extruded materials indicates that the characteristic diffractions of hematite iron oxide particles are not affected by the agglomeration process. Additionally, the hexagonal mesoscopic order of SBA-15 materials was also maintained.

As can be seen in Table 1, the percentage of iron incorporated over the powder catalysts ranged from 15 to 18 wt. %, whereas for agglomerated materials decreased up to 11-15 wt. %. This reduction is consequence of the dilution effect related to the inorganic bentonite clay incorporated into the extruded material during the agglomeration process. Moreover, the specific surface area of the agglomerated materials significantly decreased in comparison with

the powder counterparts. This phenomenon is also attributed to the amount of bentonite clay incorporated in the extruded material, which presents a low surface area (19 m^2/g), as well as the sintering process that take place during the final calcination step. Interestingly, the effect of the sintering process seems to be more important in SBA-15-based iron catalysts, which suffer 40-45 % of surface area reduction, than iron catalyst supported over non-ordered silica sol-gel materials (with reductions in the range 13-16 %). Nevertheless, iron containing catalysts based on mesostructured SBA-15 silica matrices still exhibit higher specific surface areas. Pore size distribution profiles shown in Fig. 3 for agglomerated catalysts confirm the characteristic pore size distribution of mesostructured SBA-15-type materials with a narrow pore size distribution centred at 8-9 nm, as compared to those shown by non-ordered mesoporous materials prepared by the sol-gel method with a broader pore size distribution. Unlike the physical mixture of Fe_2O_3+SBA-15(PM) which have shown the highest pore diameter (8.8 nm), the iron incorporation over SBA-15 silica support by direct synthesis or impregnation have yielded a slight reduction of the pore diameter up to ca. 7.7 and 8.2 nm, respectively. Regarding to iron catalysts supported over non-ordered mesoporous silica, the sample Fe_2O_3/SiO_2(DS) exhibits a broader pore size distribution centred at ca. 15 nm as compared to the other two catalysts of this group.

TEM images of extruded iron catalysts (Fig. 4) confirm the hexagonal arrangement of SBA-15-based materials. In both groups of iron containing catalysts, mesostructured SBA-15 and non-ordered mesoporous silica materials, the iron particle size is strongly dependent on the synthesis method and type of silica support. Interestingly, Fe_2O_3/SiO_2(DS) catalyst, prepared by the sol-gel method, evidence a remarkable dispersion of iron particles over the SiO_2 support. Unlike iron impregnated catalysts over non-ordered mesoporous silica sol-gel (Fe_2O_3/SiO_2(I)) and silica-PQ (Fe_2O_3/SiO_2-PQ(I)), impregnated Fe_2O_3/SBA-15(I) catalyst shows a better dispersion of smaller iron particles over the silica framework. These data seem to be in agreement with the small iron oxide particle sizes assumed from the X ray diffraction patterns. The presence of agglomerating bentonite layers can be also observed together with the silica support and iron oxide particles.

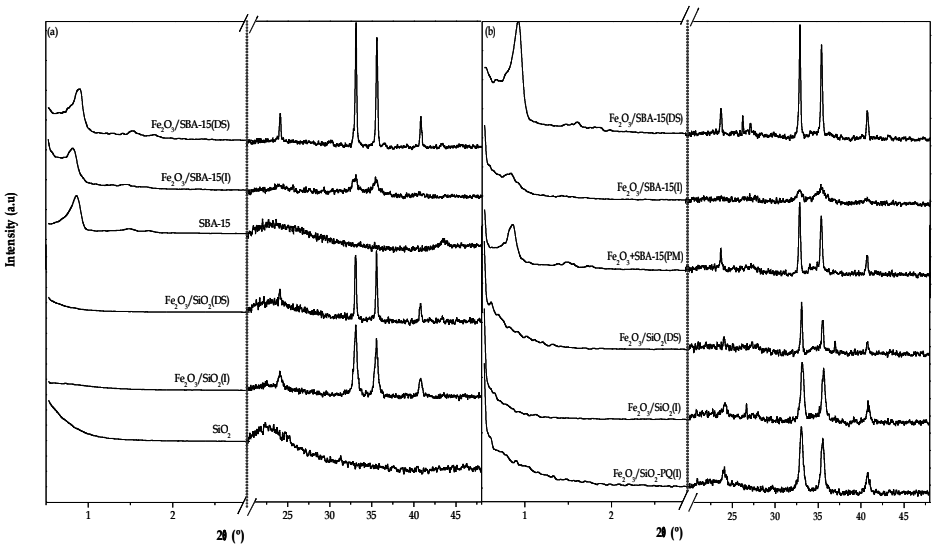

Fig. 2. XRD patterns of (a) powder and (b) extruded iron-containing materials over mesostructured SBA-15 and non ordered mesoporous silica supports.

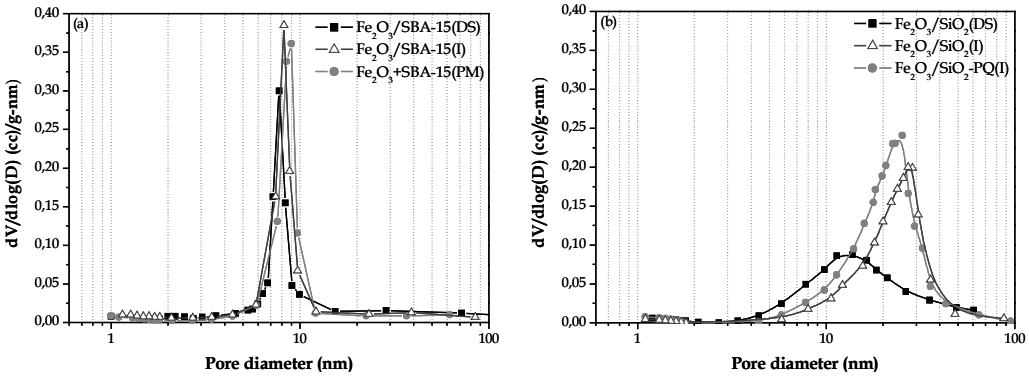

Fig. 3. Pore size distribution of the extruded materials: (a) supported over SBA-15; (b) supported over non-ordered mesoporous SiO_2.

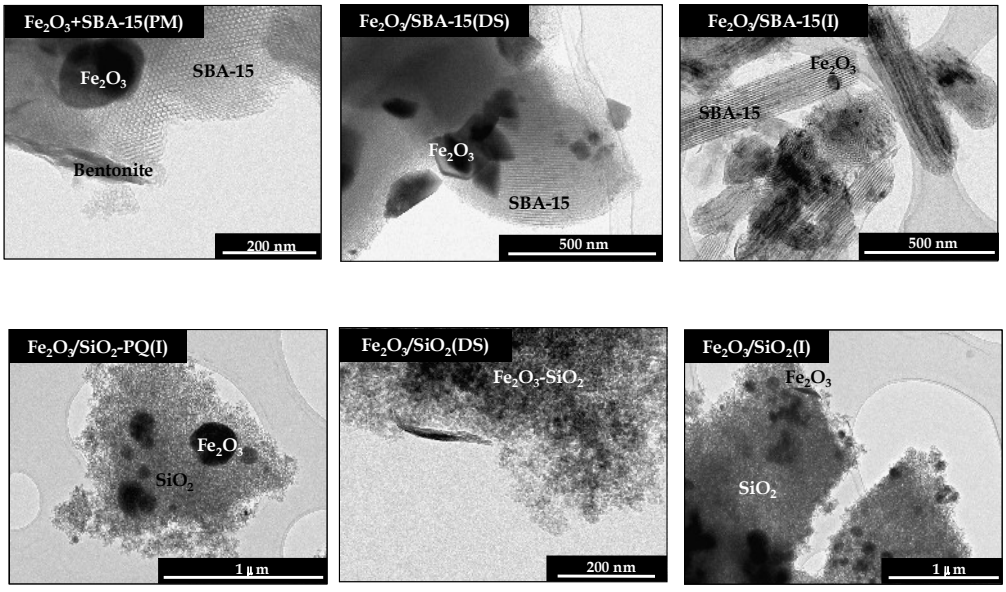

Fig. 4. TEM images of the extruded iron-containing materials.

3.2. Catalytic treatment of phenolic aqueous solutions in a fixed bed reactor

The catalytic performance of iron-containing materials for the wet peroxide oxidation of phenol aqueous solutions was evaluated in terms of TOC reduction, phenol degradation and hydrogen peroxide conversion. Likewise, the stability of the catalysts along the treatment was also studied analyzing the iron concentration leached out from the catalyst within the treated outlet effluent. Table 2 summarizes the results of the parameters monitored in the outlet stream at steady-state after eight hours of time on stream for all the synthesized catalysts.

Table 2. Activity and stability of the different iron-containing catalyst under steady-state conditions.

Catalyst	X_{TOC} (%)	X_{Phenol} (%)	X_{H2O2} (%)	η^*	$[Fe]_{leached}$ (mg/L)	pH
Fe_2O_3/SBA-15(I)	61	100	100	0.52	123	4.0
Fe_2O_3/SBA-15(DS)	64	100	100	0.56	14	4.3
Fe_2O_3+SBA-15(PM)	62	100	100	0.53	5	5.0
Fe_2O_3/SiO_2(I)	64	100	100	0.54	20	4.2
Fe_2O_3/SiO_2(DS)	52	100	100	0.44	11	4.0
Fe_2O_3/SiO_2-PQ(I)	21	93	100	0.18	120	2.3

*η = Theoretical H_2O_2 consumption/ Real H_2O_2 consumption

It is noteworthy that phenol is completely degraded for all the catalysts regardless of the silica support and synthesis method. Results of TOC evidence a high catalytic performance of SBA-15-based iron catalysts with conversions above 60 %. In the case of sol-gel materials, Fe_2O_3/SiO_2(I) keep a similar TOC conversion (64 %), whereas Fe_2O_3/SiO_2(DS) undergoes a slight reduction up to 52 %. In contrast, impregnated commercial silica PQ (Fe_2O_3/SiO_2-PQ(I)) shows a striking decrease of TOC degradation until ca. 25 %. The hydrogen peroxide is totally consumed at the operation conditions under study for all the catalysts and with similar efficiency ($\eta \approx 0.55$) except for the catalysts with lower TOC conversion previously mentioned (Fe_2O_3/SiO_2(DS) and Fe_2O_3/SiO_2-PQ(I)). Values of oxidant efficiency around 0.5-0.6 indicate an acceptable use of the oxidant. It must be pointed out that oxygenated by-products (mainly carboxylic acids) formed at high TOC degradation rates are much more refractory than phenolic compounds for its mineralization, which leads to oxidant efficiency values lower than one [21].

Nevertheless, it is particularly remarkable the significant efficiency decrease for Fe_2O_3/SiO_2-PQ(I) (η = 0.18). The lowest oxidant efficiency of Fe_2O_3/SiO2-PQ(I) could be related to the nature of the commercial silica or presence of metal traces that enable the decomposition of the oxidant to other less active radical species, different of hydroxyl radicals.

Regarding iron leaching, it is important to note that catalysts prepared by impregnation (Fe_2O_3/SiO_2(I), Fe_2O_3/SiO_2-PQ(I) and Fe_2O_3/SBA-15(I)) display higher loss of iron in the outlet stream than those prepared by direct synthesis (Fe_2O_3/SiO_2(DS) and Fe_2O_3/SBA-15(DS)). This fact indicates weaker interactions between the iron species and the silica support for iron-containing catalysts prepared by impregnation, which is not only contributed to faster catalyst deactivation but also to additional metal pollution in the treated effluent, as it is the case of Fe_2O_3/SBA-15(I) and Fe_2O_3/SiO_2-PQ(I) catalysts with iron concentrations in the outlet stream above 100 mg/L. The best stability of Fe_2O_3/SiO_2(I), as compared to the other two impregnated catalyst over mesostructured SBA-15 and mesoporous silica-PQ, indicates a stronger interaction between iron particles and silica support. This can be related to the particular physicochemical properties of the silica matrix for supporting small iron clusters. In this sense, the high density of silanol groups that typically provides silica prepared via sol-gel, could be responsible of stronger interlinking of the impregnated iron species over the silica framework.

Looking at the pH values, the decrease of the initial phenol aqueous solution pH (ca. 5.5) is observed. This decrease is normally attributed to the formation of carboxylic acids as final refractory by-products of the partial oxidation of phenol as well as protons by Fenton related reactions [22]. Some studies have reported that metal iron leaching of Fenton-like catalysts can be influenced by the solution pH in systems operating in batch conditions [12]. In this study for the continuous treatment of phenol aqueous solution with different catalysts this type of relationship was not evidenced.

The feasibility and durability of the iron catalysts for the continuous treatment of a phenol aqueous solution can be also demonstrated by the results of TOC conversion and iron leaching along the time on stream (Figure 5 and 6, respectively). TOC conversion profiles revealed times of stabilizing up to steady-state conditions ranging from 1 to 3 hours, except for the physical

mixture of Fe_2O_3+SBA-15(PM), which needs almost 7 hours. Although this enlargement of the stabilizing time has not deeply studied, this phenomenon might be related to particular diffusional constraints associated with the accessibility of the supported iron particles depending on the silica support and the type of synthesis method. Nevertheless, it must be remarked the stability of the TOC degradation rate, once the steady state is reached, up to 8 hours on stream for all the catalyst, excepting Fe_2O_3+SBA-15(PM).

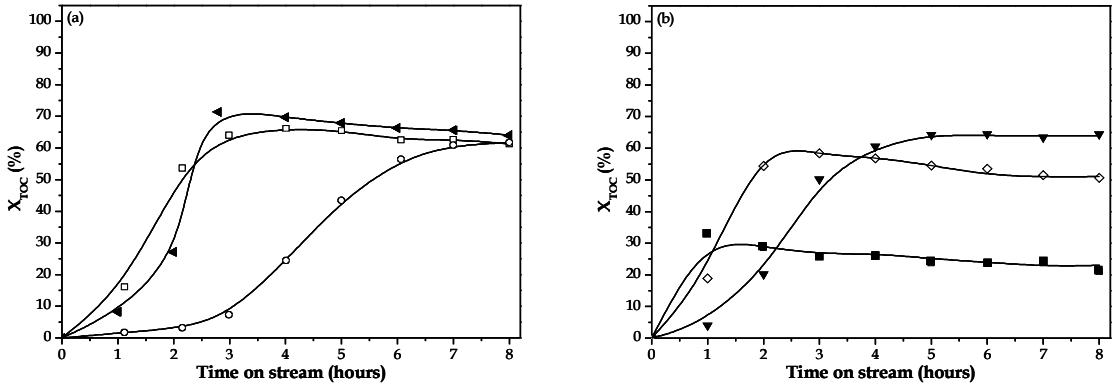

Fig. 5. TOC conversion profiles for the different iron-containing catalysts prepared by means of direct synthesis and incipient wetness impregnation: (a) -□- Fe_2O_3/SBA-15(I), -◄- Fe_2O_3/SBA-15(DS), -○- Fe_2O_3+SBA-15(PM); (b) -▼- Fe_2O_3/SiO_2(I), -◊- Fe_2O_3/SiO_2(DS), -■- Fe_2O_3/SiO_2-PQ(I).

According to the leached iron profiles (Figure 6), catalysts prepared by direct synthesis Fe_2O_3/SBA-15(DS) and Fe_2O_3/SiO_2(DS) as well as impregnated Fe_2O_3/SiO_2(I) exhibited a good behaviour with relatively low values, between 10 and 20 mg/L, and slight variation of the iron concentration detected along the time on stream. Profiles of Fe_2O_3/SBA-15(I) and Fe_2O_3/SiO_2-PQ(I) catalysts, evidence a low durability for long operating times. Attending to the legal discharge limit for iron concentration (10 mg/L), one of the main aims to apply successfully heterogeneous catalytic systems is the reduction of iron leaching to lower values, which promote higher durability of the catalyst. In this sense, the physico-chemical properties of the materials prepared by direct synthesis, independently of the used support, allow improving the catalytic stability, being consequently more interesting for this kind of applications.

Summarizing, catalysts prepared by direct synthesis over mesostructured SBA-15 and mesoporous sol-gel silica showed the best compromise over the catalytic performance, in terms

of TOC reduction, and stability, measured as iron leached out to the treated effluent. These materials provide activities above 50 % in terms of TOC conversion as well as reduced iron leaching below 15 mg/L. Although mesostructured Fe_2O_3/SBA-15(DS) catalyst presents higher values of TOC degradation (64 %) and hydrogen peroxide efficiency, the non-ordered mesoporous Fe_2O_3/SiO_2(DS) prepared via sol-gel is also considered as a potential candidate for its application in industrial catalytic wet peroxide oxidation processes. The decreased catalytic performance of Fe_2O_3/SiO_2(DS) as compared to its counterpart over mesostructured SBA-15 support could be related to its either lower iron content (11.1 vs 14 %) or lower specific surface area (225 vs 264 m^2/g).

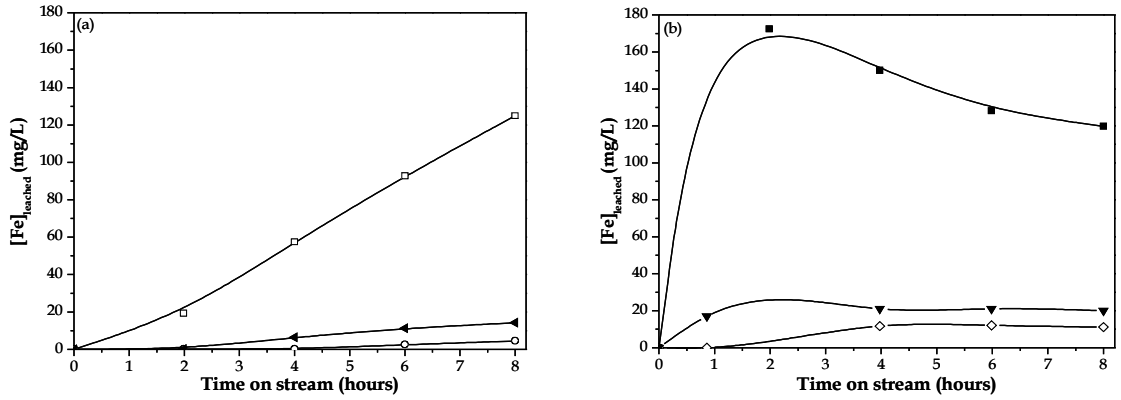

Fig. 6. Leached iron concentration for the different iron/silica catalysts prepared by means of direct synthesis and incipient wetness impregnation: (a) -□- Fe_2O_3/SBA-15(I), -◄- Fe_2O_3/SBA-15(DS), -○- Fe_2O_3+SBA-15(PM); (b) -▼- Fe_2O_3/SiO_2(I), -◊- Fe_2O_3/SiO_2(DS), -■- Fe_2O_3/SiO_2-PQ(I).

4. Conclusions

Different iron-containing catalysts based on hematite crystalline iron oxides supported over mesostructured SBA-15 and non-ordered mesoporous silica were tested in an up flow fixed bed reactor for the continuous catalytic wet peroxide oxidation of phenol aqueous solution. SBA-15 silica support provides iron catalysts with narrower pore size distributions and higher specific surface areas than non-ordered mesoporous silica. The agglomeration process do not produce significant changes in the physicochemical properties of the precursor powder catalysts, although in the case of mesostructured SBA-15 silica supports, a more accentuated reduction of the specific surface was observed.

The activity of the iron containing catalyst in terms of TOC conversion and oxidant efficiency was mainly affected by the type of silica support, whereas the iron resistance to be leached out was principally dependent on the synthesis method. The iron incorporation in the silica matrix by means of direct synthesis (co-condensation of iron and silica sources) has provided higher stability of the supported iron species. In contrast, those catalysts prepared by incipient wetness impregnation proved higher losses of iron in the treated aqueous solution (up to 100 mg/L). Mesostructured Fe_2O_3/SBA-15 is shown as the best catalyst with a high catalytic performance and reduced iron leaching for the treatment of phenolic aqueous solutions. Non-ordered mesoporous Fe_2O_3/SiO_2(DS) catalyst prepared via sol-gel in absence of organic template was also considered an interesting candidate for its application in wet peroxide oxidation processes. Both catalysts achieved a total phenol removal with TOC reductions above 50 % and relative low iron leaching (below 15 mg/L) operating for eight hours on stream.

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